HIGH PERFORMANCE MAGNETS

FINAL REPORT

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13. ABSTRACT (Maximum 200 words)

Our efforts in this project were focused on three different materials, namely; interstitial Sm-Fe carbides and nitrides, high energy product $Nd_2Fe_{14}B$ magnets with MgO addition, and nanocomposite $Nd_2Fe_{14}B/\alpha$-Fe consisting of a fine mixture of hard and soft phases. In the Sm-Fe carbides and nitrides the interstitial C and N significantly change the anisotropy and Curie temperature of the 2:17 phase and make these materials attractive for permanent magnets. Addition of Ga and Cr lead to higher amounts of C in the 2:17 phase and to large coercivities in melt spun samples with fine microstructure. In Nd-Fe-B, the addition of MgO in sintered magnets leads to a Nd-Fe-Mg-O phase surrounding the 2:14:1 grains and causes a high coercivity. The addition of grain growth inhibitors (Nb) in nanocomposite $R_{12}Fe_{14}B/\alpha$-Fe(R=Nd,Pr) magnets leads to a variety of crystallization behaviors with the discovery of metastable phases and the development of fine microstructures with high coercivity.

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INTRODUCTION

Our studies were focused on the following three main areas: (i) the search for new phases/compounds whose properties can be used for the development of high performance magnets, (ii) the use of the novel processing techniques of melt-spinning and mechanical alloying for the fabrication of nanocrystalline/nanocomposite magnets with improved magnetic properties, and (iii) the understanding of the magnetic hardening behavior of these magnets which will help us design stronger and less expensive magnets. This project has been very successful and has led to numerous publications and presentations at national meetings and conferences. A brief summary of the findings is listed below.

SUMMARY OF IMPORTANT RESULTS

1. Rare Earth-Fe(Co)-Carbides and Nitrides

Our research was focused on the 2:17-type and 3:29-type carbides and nitrides. The incorporation of interstial C and N was found to improve the magnetic properties substantially.

(i) Magnetically hard $Sm_2Fe_{17-x}Ga_xC_y$ (x = 2, 3 and y = 1, 1.5, 2, 2.5) ribbons were prepared with a high coercivity of 12.8 kOe at room temperature. The high coercivity obtained in this study may be attributed to the addition of Ga, which allows a higher solid solubility of carbon in the samples with a corresponding increase in the anisotropy field. Microstructure studies revealed the coexistence of an α-Fe and a 2:17 type phase. In samples annealed at high temperatures, the distribution of these phases is inhomogeneous, with a course grain size leading to a shoulder in the demagnetization curve. However, in samples annealed at lower temperatures (700°C) the grains are finer and uniform, leading to a smooth demagnetization curve with a lower coercivity but with a higher reduced remanence, which are characteristic of nanocomposite exchange-coupled magnets.

(ii) The R_2Fe_{17}-type $Sm_2Fe_{14-x}Co_xSi_2$ compounds with x = 0 to 7 crystallize in Th_2Zn_{17}-type structure. Substitution of Co leads to an increase in Curie temperature from 514 K for x = 0 to 817 K for x = 7. It also enhances the uniaxial anisotropy that changes from planar in $Sm_2Fe_{14-x}Co_xSi_2$ to uniaxial for x $\geq$4. The $Sm_2Fe_{14-x}Co_xSi_2N_y$ nitrides maintain the Th_2Zn_{17}-type structure but with a unit-cell expansion $\Delta V/V$ up to 5% compared to the host materials. The $Sm_2Fe_{14-x}Co_xSi_2C_z$ carbides with z = 1 maintain the Th_2Zn_{17}-type structure, and transform to the $BaCd_{11}$-type structure for z = 2. The room-temperature anisotropy field obtained is 100 kOe for $Sm_2Fe_{14}Si_2C$ and 17 kOe for $Sm_2Fe_{10}Co_4Si_2N_{2.3}$. A very large anisotropy field is also observed at low

temperature (1.5 K) with a value of 204 kOe for $Sm_2Fe_{14}Si_2C$ and 276 kOe for $Sm_2Fe_{10}Co_4Si_2N_{2.3}$.

(iii) $Sm_3(Fe_{0.933}Ti_{0.067})_{29}N_5$ and the parent compounds crystallize in the $Nd_3(Fe,Ti)_{29}$-type structure. These compounds exhibit a ferromagnetic coupling with a Curie temperature of 750 K and a saturation magnetization of 157 e.m.u.g^{-1} at 4.2 K. $Sm_3(Fe_{0.933}Ti_{0.067})_{29}$ compounds exhibit uniaxial anisitropy from 4.2 K to the ordering temperature. The anisotropy field is 12 T at room temperature and 25 T at 4.2 K. The nitrides and carbides studied here all have excellent intrinsic magnetic properties and can be new candidates for permanent magnet development.

2. Nd-Fe-B Magnets with MgO Addition

In this work we have studied in detail the effect of MgO on the magnetic properties and intergranular microstructure. We have found that both coercivity and thermal stability can be remarkably enhanced by the intergranular addition of MgO. For $Nd_{22}Fe_{71}B_7$ magnets with 2 wt % MgO addition, the coercivity at room temperature and 180°C are enhanced from 17.0 and 3.2 kOe to 22.1 and 5.2 kOe respectively, and the reversible and irreversible flux loss from room temperature to 180°C is reduced from 25.4% and 5.2% to 20.5% and 0.5%, respectively. Microstructural studies reveal that a new intergranular Nd-O-Fe-Mg phase with a composition close to $Nd_{70}O_{23}Fe_3Mg_2$ appears in magnets with the addition of MgO. The improvement of magnetic properties by the addition of MgO is believed to be due to the appearance of the Nd-O-Fe-Mg intergranular phase, which probably hinders the propagation of the domain walls between $Nd_2Fe_{14}B$ grains. It is further found that the addition of Mg or O alone into the intergranular regions of the magnets does not lead to the formation of this Nd-O-Fe-Mg intergranular phase, and thus, cannot substantially improve the coercivity and the thermal stability of the magnets.

3. Nanocrystalline/Nanocomposite Magnets

These magnets consist of a fine mixture of hard and soft phases that are exchange-coupled to lead to a magnet with higher magnetization, higher remanence, and energy product.

(i) $Pr_2Fe_{14}B/\alpha$-Fe

Nanocomposite $Pr_2Fe_{14}B/\alpha$-Fe magnets have been synthesized by melt-spinning a $Pr_8Fe_{86}B_6$ alloy at low wheel speed in the range from 10 to 22 m/s. Microstructural and magnetic studies showed that there is an optimum wheel speed (about 17 m/s) at which a uniform $Pr_2Fe_{14}B/\alpha$-Fe microstructure with fine α-Fe grains is developed directly from the melt. Lower speed leads to larger grains for both the 2:14:1 and α-Fe, while higher speed leads to the appearance of an amorphous phase that will result in a $Pr_2Fe_{14}B/\alpha$-Fe structure with larger α-Fe grains after a subsequent crystallization annealing. Magnetic properties obtained under the optimum-quenching followed by a subsequent annealing

are $M_s = 176.6$ emu/g, $M_r = 118.2$ emu/g, $M_r/M_s = 0.67$, $H_c = 5.4$ kOe and $(BH)_m = 12.6$ MGOe. The coercivity and energy product are about 20% higher than those obtained by over-quenching and then annealing due to the refinement of α-Fe size that leads to an enhanced exchange coupling between $Pr_2Fe_{14}B/\alpha$-Fe. The fine α-Fe development is associated with its solidification behavior characterized by higher nucleation rate and lower growth rate during the rapid solidification.

(ii) $R_2(Fe, Co, Nb)_{14}B/(Fe, Co)$ (R = Nd, Pr)

Nanocomposite $R_2(Fe,Co,Nb)_{14}B/(Fe,Co)$ (R = Nd, Pr) magnets prepared by crystallizing the as-made $R_8(Fe,Co,Nb)_{86}B_6$ amorphous melt-spun ribbons have been studied. The coercivity is found to depend mainly on the grain size of the soft phase that is very sensitive to the sample composition. The average grain size is about 30 nm in $R_8F_{86}B_6$, but the microstructure is not homogeneous and there are several large α-Fe grains with sizes up to 50-100 nm. The coercivities are 3.3 kOe in $Nd_8Fe_{86}B_6$ and 4.9 kOe in $Pr_8Fe_{86}B_6$ samples. Nb substitution significantly reduces the grain size of α-Fe and increases the coercivity. The highest coercivities obtained are 5.5 kOe in $Nd_8(Fe_{0.97}Nb_{0.03})_{86}B_6$ and 9.3 kOe in $Pr_8(Fe_{0.92}Nb_{0.08})_{86}B_6$ samples. Co substitution for Fe increases the grain size of both the 2:14:1 phase and α-Fe and dramatically decreases the coercivity. Increasing the B content in Co substituted samples leads to the formation of a more homogeneous and finer microstructure and thus to a partial recovery of the coercivity from 2.3 kOe in $Nd_8(Fe_{0.5})Co_{0.5})_{0.97}Nb_{0.03})_{86}B_6$ to 4.3 kOe in $Nd_8(Fe_{0.5}Co_{0.5})_{0.97}Nb_{0.03})_{82}B_{10}$ and from 2.1 kOe in $Pr_8(Fe_{0.5}Co_{0.5})_{0.94}Nb_{0.06})_{86}B_6$ to 6.5 kOe in $Pr_8((Fe_{0.5}Co_{0.5})_{0.94}Nb_{0.06})_{82}B_{10}$. It is further found that Co substitution improves the temperature dependence of the saturation magnetization.

(iii) $Sm(Co,Fe,Cu,Zr)_zM_x$

The objective of this study was to produce a nanocrystalline $Sm_2(Co,Fe,Cu,Zr)_{17}$, magnet consisting of magnetically hard $Sm_2Co_{17}/SmCo_5$ phases and soft Fe (Co) phases. For this we have prepared melt-spun ribbons of $Sm(Co_{0.65}Fe_{0.28}Cu_{0.05}Zr_{0.02})_zB_x$ with z = 7.0, 7.7, 8.5, 9.0, x = 0, 0.5, 1.0, and $Sm(Co_{0.60}Fe_{0.23}Cu_{0.05}Zr_{0.02}C_{0.1})_z$ with z = 7.7, 8.5, 9.0 and 9.5 and determined their crystallization temperatures, crystal structure, structure morphology and magnetic properties. It was found that the magnetic properties were very sensitive to the nominal composition and processing parameters. Increasing the boron content from x = 0.5 to x = 1.0 resulted in samples with higher α-Fe content and reduced coercivity. Energy products up to 8 MGOe and reduced remanence as high as 0.72 were observed. In general, the boron containing samples gave higher values of coercivity and of reduced remanence because their microstructure was finer.

(iv) Exchange Spring Behavior

The magnetic properties of nanocrystalline melt-spun single phase ($Nd_2Fe_{14}B$-type) and composite ($Nd_2Fe_{14}B$ + α-Fe) magnets have been studied systematically in an attempt to better understand their 'exchange spring' behavior. The reversibility of the recoil demagnetization curves has been found to increase with increasing content of the

soft phase giving rise to the characteristic exchange spring behavior only in nanocomposite samples. δM plots indicate positive interactions of the exchange type for small fields; for fields higher than the remanence coercivity, magnetostatic interactions become dominant. The relative strength of the magnetostatic interactions is increased in samples with higher soft phase contents.

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